

# En Chem, Inc.

## Quality Assurance Document

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REVISION NO. 12  
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### STANDARD OPERATING PROCEDURE

TITLE: Total Organic Carbon Analysis

DEPARTMENT: Inorganic - Wet Chemistry

APPLICATION: Determination of organic carbon in soil, sludge and solid waste.

REFERENCE: EPA Manual SW846, 3rd Edition, Method 9060 Modified  
Dohrmann DC-190 High Temperature TOC Analyzer Operating Manual,  
September 1994 Revision C

#### PROCEDURE SUMMARY:

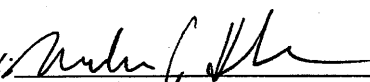
Inorganic carbon from carbonates and bicarbonates is removed by acid treatment. The sample is vaporized and swept by the continuous oxygen flow to the 800 °C combustion zone where all carbonaceous matter is oxidized to CO<sub>2</sub>. The carbon dioxide is bubbled through an acidified liquid and then routed through a mist trap which together serve to remove any entrained water and scrub out any corrosive species formed. Finally, the gas is swept to the linearized non-dispersive infrared detector which is made specific for CO<sub>2</sub> measurement.

#### LABORATORY DETECTION AND REPORTING LIMITS:

Soil: LOD EQL  
91 mg/kg 500 mg/kg

Approximate working range of method: LOD to 30,000 mg/kg.

APPROVED BY

  
Michael J. Helmann  
Wet Chemistry Group Leader

8/3/01  
Date

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Julie A. Trivedi  
Quality Assurance Officer

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Date

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Glen A. Coder  
Laboratory Manager

\_\_\_\_\_  
Date

#### Annual Review

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| Date:     |  |  |  |  |  |
| Initials: |  |  |  |  |  |

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### SAMPLE HANDLING & PRESERVATION:

The sample is collected in a glass jar and refrigerated at 4°C. The recommended holding time is 28 days from sample collection.

### SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Materials Safety Data Sheets (MSDS) for information on specific chemicals.

### INTERFERENCES:

Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation. Removal of carbonate and bicarbonate by acidification can result in the loss of volatile organic substances resulting in a low bias.

Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4°C and analyzing within the specified holding time.

### APPARATUS:

Dohrmann Model 183 Total Organic Carbon Analyzer or equivalent  
Syringes: 100 µL  
Volumetric flasks: 100 mL  
Forceps  
Watch glass  
Small spatula  
Platinum boat  
Crucibles  
Magnetic stir bars  
Magnetic stir/hot plate  
Aluminum dishes  
Spatulas  
Balances: top loader, analytical capable of 0.1 mg resolution and accuracy

### REAGENTS:

Milli-Q deionized water  
Potassium hydrogen phthalate (KHP), primary standard grade  
Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)

Prepare potassium hydrogen phthalate, 2000 ppm carbon, as follows:  
Dissolve 425 mg KHP in 100 mL Milli-Q water.  
Store in an amber bottle and refrigerate. Shelf life is one month.

NOTE: Another 2000 ppm standard is prepared from a second source that is used as the ICV/CCV. Prepare calibration standards daily.

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Prepare sulfuric acid solution, 5% (v/v), as follows:

Dilute 10 mL of concentrated  $H_2SO_4$  to 200 mL with Milli-Q water, slowly adding the acid. Mix well and place in a glass bottle. Shelf life is 1 year.

Prepare Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB) and Preparation Blank (Method Blank):

Use the same D.I. water that was used for the preparation of the standards. Inject 40  $\mu$ L onto an Ottawa sand (40 mg) which has gone through the same sample preparation procedures.

Prepare Laboratory Control Sample (LCS):

Use potassium hydrogen phthalate stock standard with a concentration of 2000 ppm. Inject 19  $\mu$ L (results in a 950 mg/L spike for the LCS) into the boat.

PROCEDURE:

A. Sample Preparation

1. Place a representative homogeneous sample, at least 10 grams, in a crucible. Add a stir bar.
2. Place on a stirring hot plate. Slowly add 5%  $H_2SO_4$ , dropwise, until sample is saturated and stir bar turns freely.

NOTE: Sample will effervesce in the presence of inorganic carbon.

3. Set temperature at  $\sim 70^\circ C$  to help drive the reaction.

NOTE: Process a blank using Ottawa sand for each 20 samples prepared.

4. Check sample pH occasionally. pH should be maintained at  $<2$ . If pH is  $>2$ , add more acid.
5. Continue to heat, stir, and add acid until effervescence is no longer visible or no longer than 24 hours.

NOTE: This can be difficult to determine in some samples. Check by removing from stirring hot plate and allow to sit for several minutes. Swirl sample and look for air bubbles.

6. Dry in an oven at  $103-105^\circ$  overnight.

B. Sample Analysis

1. Set up instrument. See EN CHEM SOP WCM-18.
2. The boat is introduced into the furnace and allowed to "bake-out".
3. Refer to SOP EN CHEM WCM-18 for set up of Soils/Boat.
  - a. Set instrument to NPOC/BOA mode. After the furnace has warmed up to the set temperature, have a prepared boat ready to inject. Place the boat

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in the slide. Close the lid. Press start. Type in the mass of the of the sample. Hit Enter. Wait until the inject light comes on.

- b. When the unit chimes, inject/slide the sample/standard. It will chime again when it is finished. Enter Y or N for replicate. Print the analysis if N.
- c. Continue on to the next sample or standard.

### Calibration

- 4. Calibrate the instrument as follows:
  - a. Using a 2000 ppm KHP standard, inject 40  $\mu$ L of the standard into the boat by lifting the cover to the sample port.
  - b. Close the cover, hit start and enter the weight as 40 mg. Hit Enter. Wait for chime, then push sample in via the magnet.
  - c. Instrument will chime when analysis is complete. Pull magnet back.
  - d. Allow sample boat to cool a minute or two.
  - e. Repeat standard injection two more times.
  - f. When three calibration standards are read, Press NO to continue. The instrument will calculate a mean and standard deviation. To update the calibration factor, push the calibration button. Find and select the Update Calibration Factor (#5). Press #5 and the unit will scroll to it and update. Write this factor down. Continue to calibrate with the next standard.

### Analysis QC

- 5.
  - a. Analyze a 500, 1000, 2000 and 3500 ppm standards from the same source as the calibration. The % recovery for each standard must be  $\pm 10\%$  of the true value. Then analyze an ICV sample, which must be  $\pm 10\%$ .
  - b. The ICB value should be less than the detect value The ICB must be analyzed after the ICV. The absolute value must be less than the (EQL).
  - c. LCS: Weigh 10 mg of the dried ottawa sand using the analytical balance. Add 19  $\mu$ L of the 2000 ppm std and analyze. This value must fall within the in-house generated control limits of 86-130%.
  - d. Blank: Weigh out 10 mg of the dried Ottawa sand using the analytical balance and add 40  $\mu$ L of the Milli-Q water and analyze. The method blank concentration should be less than the EQL. If the MB concentration is greater than the EQL, all associated samples will be re-analyzed unless the sample concentrations are greater than 20x the MB concentration. If MB concentration is between MDL and EQL, samples will be qualified with an A flag unless the sample concentration is greater than 20x the MB

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concentration. If the MB fails these criteria, analysis should be stopped, and the problem should be identified and corrected before analysis can resume.

### Samples

6. Weigh a well-mixed, dry, homogeneous sample into a platinum boat using an analytical balance.

NOTE: Sample size should be 10 mg.

7. Place the sample in the saddle and close the injection port.
8. Push "START" and type in the mass. Hit enter. Wait until the unit beeps before adding the sample boat into the furnace. The red light on the unit will move from WAIT to INJECT to ACQUIRE. Unit will chime when finished. Remove the boat to the solid metal block to cool before proceeding.

NOTE: Each soil sample must be analyzed with a minimum of 2 replicates. If the RPD between the 2 replicates is within 0-20%, then the average of the 2 replicates can be reported. If the RPD is >20%, a third replicate must be analyzed and the average of the three replicates would then be reported.

If Quadruplicate analysis is required for all samples. Each sample will be composed of 4 individual 10 mg analyses. Report all four individual readings and the average of the four readings. The method citation will still be SW846 9060.

For Quad analysis: The ICV, CCV, ICB, CCB, LCS and MB do not need to be read in quadruplicate, but the MS/MSD does if requested by client.

- C. Shutdown  
Follow SOP WCM-18.

### QUALITY CONTROL

#### Calibration Check Standard

Three standards are analyzed immediately after calibration to verify linearity. All must be from the same source as the calibration standard and meet the control limit of  $\pm 10\%$  of the true value.

#### Replicates

Replicates should meet a %RPD of 20. If not, read a third aliquot of sample.

#### Initial Calibration Verification (ICV)

The ICV must be run immediately after the three calibration check standards and must meet control limit of  $\pm 10\%$  of the true value. If not, recalibrate.

#### Initial Calibration Blank (ICB)

The ICB must be analyzed after the ICV. The absolute value of the ICB must be less than the estimated quantitation limit (EQL). If the ICB is outside of the control criteria, sample analysis should not proceed. Correct the problem and recalibrate the instrument.

**Method Blank (MB)**

The MB is carried through all prep procedures and analyzed with a frequency of 5%. The method blank concentration should be less than the EQL. If the MB concentration is greater than the EQL, all associated samples will be re-analyzed unless the sample concentrations are greater than 20x the MB concentration. If MB concentration is between MDL and EQL, samples will be qualified with an A flag unless the sample concentration is greater than 20x the MB concentration. If the MB fails these criteria, analysis should be stopped, and the problem should be identified and corrected before analysis can resume.

**Laboratory Control Sample (LCS)**

An LCS consisting of known concentration must be prepared and analyzed for each batch of 20 samples, and meet the current control limits of 86-130%. If the LCS recovery is outside of the control limits, the system is out of control. Terminate the analysis and identify the problem. Once the problem has been corrected, the samples should be re-prepared and analyzed.

**Continuing Calibration Verification (CCV)**

The CCV is analyzed after every 10 analytical samples. It must be from a second source and must meet current control limits of  $\pm 10\%$  of true value. If not, the calibration procedure must be repeated and all samples since the last successful CCV must be reanalyzed.

**Continuing Calibration Blank (CCB)**

The CCB is analyzed after every CCV and must be less than the absolute value of the EQL. If not, the instrument must be re-calibrated, and all samples since the last acceptable CCB must be reanalyzed.

**Matrix Spike/Matrix Spike Duplicate**

A matrix spike/matrix spike duplicate must be performed on each group of samples of a similar matrix type with a frequency of 5%. The recovery should be within the current in-house generated control limits of 35-155%. In addition, the RPD should be less than 16. If either of the recoveries or the RPD are outside of the control limits, the results will be flagged.

**Calculation:**

The instrument provides calculated sample results in mg/kg, calculations are only necessary if a dilution was used.

Raw Data Value (mg/kg) x Dilution Factor = TOC (mg/kg)

**ACCURACY:**

A matrix spike and matrix spike duplicate must be performed on each group of samples of a similar matrix type with a frequency of 5% and meet the current control limits for accuracy.

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Spike calculation:

$$\% \text{ Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}}$$

SSR = Spiked Sample Result  
SR = Sample Result  
SA = Spike Added

If there is insufficient volume available for an MS/MSD, perform an LCS/LCSDUP.

### PRECISION:

A matrix spike duplicate must be analyzed on each group of samples of a similar matrix type with a frequency of 5% and meet the current control limits for precision.

Use relative percent difference (RPD) calculation:

$$\text{RPD} = \frac{|\text{MS} - \text{MSD}|}{(\text{MS} + \text{MSD})/2} \times 100$$

MS = Matrix Spike Value  
MSD = Matrix Spike Duplicate Value

If there is insufficient volume available for an MS/MSD, perform an LCS/LCSDUP.

### POLLUTION PREVENTION and WASTE MANAGEMENT:

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order and prepare only those quantities of reagents that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.

### SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Materials Safety Data Sheets (MSDS) for information on specific chemicals.